

Phase behavior of model mixtures of colloidal disks and polymers

Martin A. Bates and Daan Frenkel

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

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The phase behavior of model colloidal systems containing platelets and polymer is investigated using computer simulation and perturbation theory. For polymer coils with a diameter σ_p larger than $0.3\sigma_D$, where σ_D is the diameter of the platelets, isotropic fluid-fluid coexistence is observed, in addition to the usual isotropic-nematic transition for hard disk systems. For very small polymer coils ($\sigma_p < 0.1\sigma_D$), a nematic-nematic demixing transition is observed, although this occurs at extremely high platelet density. The case of colloidal platelets and thin stiff rods is also examined. Demixing is observed in the isotropic phase for long rods and in the nematic phase for short rods, as for large and small polymer coils, respectively. However, the nematic-nematic demixing transition for platelet-rod mixtures occurs at a much lower platelet density than in the platelet-disk mixtures.

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I. INTRODUCTION

It is well known that an effective attractive force can be induced in a suspension of hard body, colloidal particles by the addition of a smaller species [1–5]. The influence of this attractive force on the phase behavior has been studied experimentally using mixtures of spherical colloids [1,2] and colloids plus nonadsorbing polymer [3–5] and it is found that the nature of the phase diagram depends on the size ratio of the large and small particles. The range and depth of the depletion-induced attractions can be modified by changing the size and concentration of the smaller species, respectively, and so the phase diagram can be modified in a systematic way. In this paper, we will concentrate explicitly on systems composed of colloids and polymer, in which the polymer coils act as a “soft” depleting agent.

The depletion interaction in colloid- and free polymer systems was first described by Asakura and Oosawa [6]. The depletion forces arise in these mixtures, since the smaller polymer coils are excluded from a narrow shell or depletion zone of the order of their radius around the larger particle. If two of the larger particles are in close proximity then their depletion zones overlap. This leads to an increase in the total volume available for the polymer and so to an effective attraction between the larger particles [6]. Meijer and Frenkel [7] have studied depletion interactions in a computer simulation study of colloids and polymers. Their results showed that the Asakura and Oosawa model [6] for colloid-polymer suspensions, which approximates the free polymer coils by mutually interpenetrable spheres that cannot penetrate the colloid, gives a good approximation to the interaction between the particles as long as the radius of gyration of the polymer is less than 70% of the radius of the colloid. This behavior had earlier been predicted on the basis of perturbation theories by Gast, Hall, and Russel [8] and the theoretical approach was subsequently refined by Lekkerkerker *et al.* [9]. The depletion effect is not restricted to spherical particles. Mixtures of rod-shaped particles and polymer have been studied experimentally and have been shown to exhibit a rich phase behavior. For such mixtures, many possibilities occur since small particles can act as a depletion agent for

large rods or small rods can induce effective attractions between large spheres. Especially in the latter case, a wide variety of complex morphologies can occur when the rods are at a high enough concentration to exhibit liquid crystalline phases [10]. Models for these systems have also been studied by simulation and perturbation theory [11–14] but the structures of the complex phases are still not completely understood. Experiments on systems of pure colloidal disks have been reported only recently [15,16], and the influence of realistic features such as size polydispersity on the phase behavior of these systems is also starting to be understood [17,18]. The possibility of rich liquid crystalline behavior exhibited by mixtures containing disks has yet to be fully investigated although a start has been made [19]. In this paper, we examine the phase behavior of platelet-polymer and platelet-rod mixtures using computer simulation and perturbation theory.

II. SIMULATION OF COLLOIDAL PLATELETS PLUS POLYMER

In our simulations, we model the colloidal platelets using infinitely thin disks. This model has previously been used to investigate the phase behavior of systems of monodisperse [17,20] and polydisperse [17] colloidal disks since it is particularly cheap to use in computer simulations. However, it does have the drawback that only isotropic and nematic phases can be observed and that translationally ordered phases such as the columnar liquid crystalline phase are not present at finite densities. Since many of the colloidal dispersions studied experimentally to date have rather low number density, this is not necessarily a problem. The polymer coils are modeled in the spirit of Asakura and Oosawa [6], using spheres which cannot penetrate the disks but are mutually interpenetrable. Simulations were performed at constant polymer fugacity using an osmotic equilibrium model [14], in which a reservoir of polymer at chemical potential μ_p is in equilibrium with a platelet-polymer mixture. Within this approximation the fugacity of the polymer $z_p = \exp(\beta\mu_p)/\Lambda^3$ in the system of platelets is equal to the pressure of the ideal polymer reservoir; here $\beta = 1/kT$ is the in-

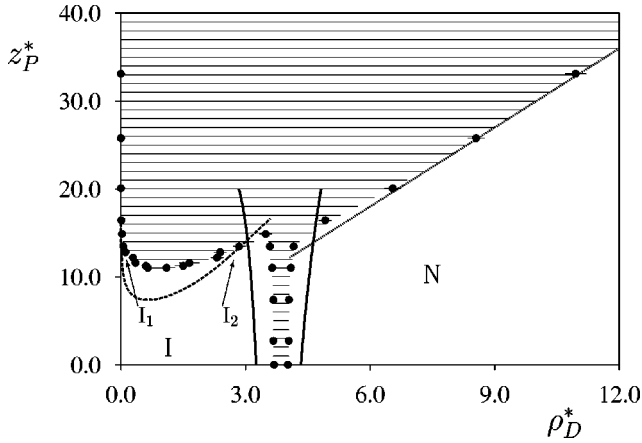


FIG. 1. Phase diagram for mixtures of colloidal disks (hard platelets) and polymer coils (penetrable spheres) as a function of platelet density, ρ_D^* , and polymer fugacity, z_p^* . (●) Simulation results obtained from Gibbs ensemble and grand canonical simulations for $\sigma_p = 0.5\sigma_D$ (Sec. II). The coexistence regions obtained from the simulations are indicated by horizontal shading. The dashed line indicates the results of the perturbation theory (Sec. III) for coexistence between the I_1 and I_2 isotropic phases for $\sigma_p = 0.5\sigma_D$. The solid lines indicate the location of the nematic-isotropic transition. The dotted line shows the nematic equation of state $z_p^* = P^* = 3\rho_D^*$ for a system of pure disks (Sec. III).

verse temperature and Λ is the thermal de Broglie wavelength [21]. For the low platelet density region of the phase diagram, Gibbs ensemble simulations [21] were found to be an efficient way to determine the coexistence densities. At higher platelet densities in the vicinity of the nematic-isotropic (NI) transition, the Gibbs ensemble method becomes sluggish even for pure disk systems [18]. A more efficient route to the coexistence densities is the determination of the equation of state using grand canonical simulations, since these simulations avoid volume changes that are much less efficient than particle insertions for this system [18]. Fortunately, hysteresis is minor at the NI transition and so the coexistence densities can be determined within a few percent directly from the equation of state and further free-energy calculations are not necessary. We therefore also use grand canonical ensemble simulations to determine the phase behavior of the model platelet plus polymer systems. The equation of state is determined at fixed μ_p^* while varying μ_D^* , the chemical potential of the disks. Simulation results are shown in Fig. 1 for polymer coils with diameter $\sigma_p = 0.5\sigma_D$, where σ_D is the platelet diameter. For zero polymer fugacity, the system exhibits a weakly first-order NI transition at $\rho_D^* = N\sigma_D^3/V \approx 4$. Increasing the polymer fugacity has little effect on the phase behavior until $z_p^* \approx 10$, when an isotropic fluid-fluid (I_1I_2) transition is induced, equivalent to that observed in mixtures of spheres [1–5]. The width of the NI transition broadens slightly with increasing polymer fugacity. This eventually ends in an I_1I_2N triple point, above which there is coexistence between a very low-density isotropic phase I_1 and the nematic. In principle, computer simulation could be used to determine the phase diagram as a function of polymer diameter and thus the influence of the size of the polymer on the phase behavior. However, this would be computationally expensive and so in the next sec-

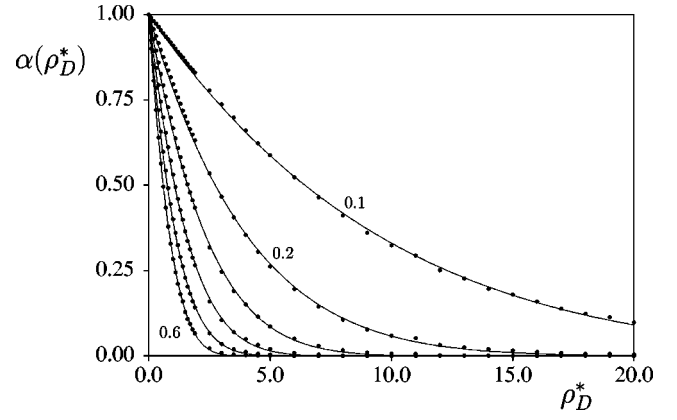


FIG. 2. The free volume fraction, $\alpha(\rho_D^*)$, for spheres of diameter σ_p as a function of platelet density, ρ_D^* . The relative sphere diameter (σ_p/σ_D) from top to bottom is 0.1 to 0.6 in steps of 0.1.

tion we seek an alternative route to this information.

We note that all quantities are quoted in reduced, dimensionless units; these are, platelet density $\rho_D^* = \rho_D \sigma_D^3$, pressure $P^* = P \sigma_D^3/kT$, chemical potential $\mu^* = \mu/kT$ and fugacity $z^* = z \sigma_D^3$.

III. DETERMINATION OF THE PHASE DIAGRAM BY PERTURBATION THEORY

The theoretical formalism used to determine the phase diagram follows that developed by Lekkerkerker *et al.* [9,12] used to study the phase behavior of colloidal mixtures containing rods and spheres [11–14]. The perturbation theory is based on the construction of the grand potential, which is a function of the polymer fugacity, for the system of interest. Since this has been discussed in detail elsewhere [11–14], here we merely quote the result that the (osmotic) pressure P_D^* and the chemical potential μ_D^* of the disks in the mixture are

$$\beta P_D^* = \beta P^* + z_p^* \left(\alpha - \rho_D^* \frac{\partial \alpha}{\partial \rho_D^*} \right) \quad (1)$$

and

$$\beta \mu_D^* = \beta \mu^* - z_p^* \frac{\partial \alpha}{\partial \rho_D^*}, \quad (2)$$

respectively, where P^* and μ^* are the pressure and chemical potential in the pure disk system and α is the free volume fraction available to the polymer coils (interpenetrable spheres); we reserve the symbols with no subscripts to refer to data obtained in the pure disk system. In previous studies of spheres in rod-based system [12], scaled particle theory was used to provide the required free volume fraction α . For the disk system, this is not known analytically and so we have determined this, as a function of sphere diameter and platelet density, by simple insertion of spheres into a pure disk system. The results are shown in Fig. 2. At zero platelet density, the entire volume is accessible to polymer and so $\alpha = 1$. As the density is increased, α drops as the available space decreases; clearly this is more rapid for larger spheres than for smaller ones. We observe that there is essentially

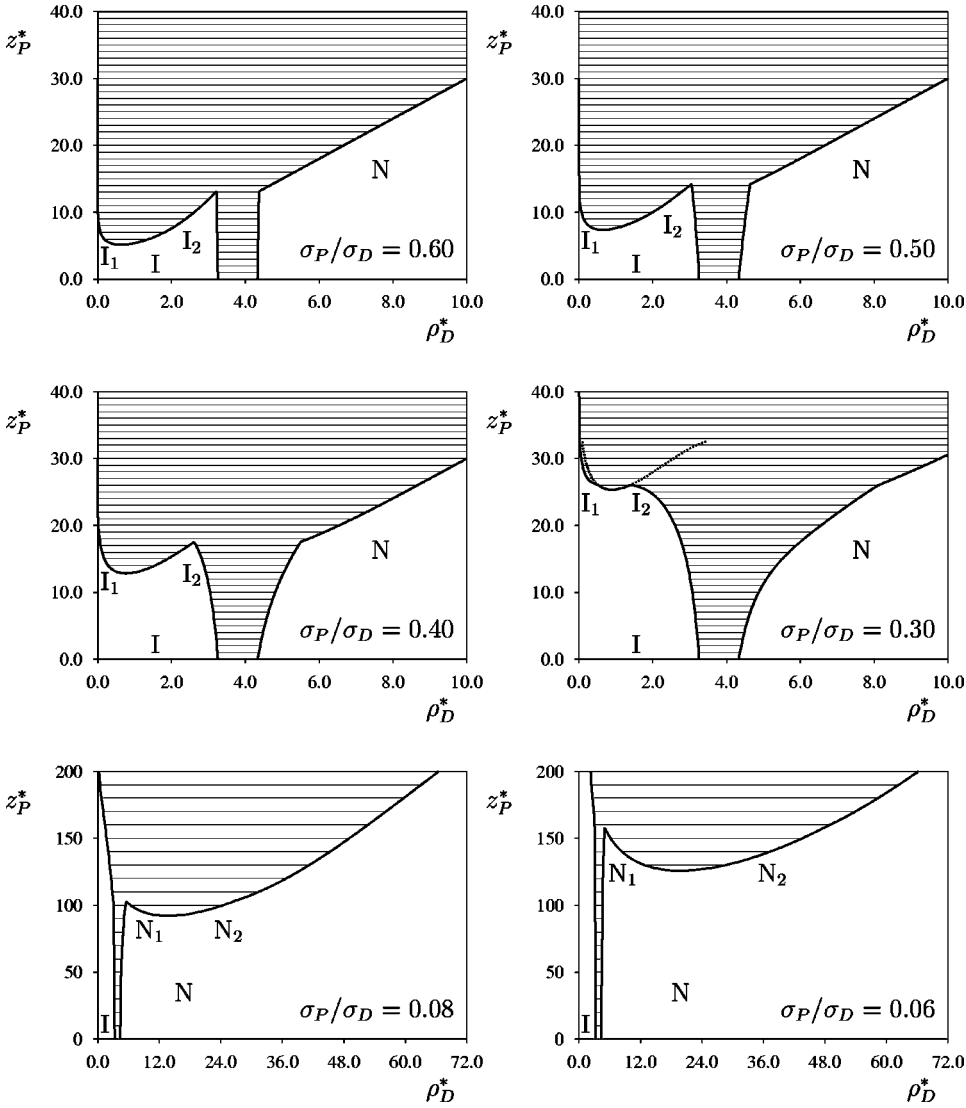


FIG. 3. Phase behavior of hard platelet and polymer (penetrable spheres) mixtures as predicted by perturbation theory as a function of platelet density, ρ_D^* , and polymer fugacity z_P^* for various relative sphere diameters (σ_P/σ_D).

very little available volume to insert spheres of diameter $\sigma_P = 0.5\sigma_D$ at platelet densities in the vicinity of the NI transition ($\rho_D^* \approx 4$). For each polymer diameter, the free volume fraction was found to possess a functional form very similar to that arising from scaled particle theory for large and small spheres, and so for convenience the α used in Eqs. (1) and (2) was fitted to

$$\alpha = (1 - a\rho_D^*) \exp\left(\frac{-b\rho_D^*}{1 - a\rho_D^*}\right), \quad (3)$$

in which a and b were taken to be adjustable parameters used to fit the curves in Fig. 2. The other input required for the perturbation theory is the equation of state of the pure disk system. This has been determined in previous simulation studies [17,18,20] and so is known numerically to quite a high accuracy. However, rather than fit somewhat arbitrary functions to the numerical data, we use the five-term virial expansion for the isotropic phase and the equation $P^* = 3\rho_D^*$ for the nematic phase, both of which have been shown to give very good agreement with the numerical data, except very close to the transition [20]. Figure 1 shows the I_1I_2 coexistence densities for mixtures of platelets with

spheres of diameter $0.4\sigma_D$ and $0.5\sigma_D$, in addition to those for the NI coexistence for $\sigma_P = 0.5\sigma_D$. Clearly, the NI transition is predicted to be too wide, even for the pure disk system in which $z_P^* = 0$. This occurs since the five-term virial expansion and the equation $P^* = 3\rho_D^*$ slightly over and underpredict the pressure in the isotropic and nematic phases, respectively [20]. However, for simplicity we use these forms of the equation of state bearing in mind that the true NI transition is not so strong. The predicted NI transition is seen to widen slightly with increasing z_P^* , in agreement with the simulation data. The coexistence between the I_1 and I_2 isotropic phases is also predicted by the perturbation theory. Although the agreement with the simulation data is not perfect, the theory does give reasonable results; the predicted critical point for $\sigma_P = 0.5\sigma_D$ occurs at lower z_P^* than observed in the simulation and at possibly very slightly lower ρ_D^* . The final part of the phase diagram is coexistence between the N and I_1 phases at high z_P^* . At high densities in the nematic phase, spheres of diameter $0.5\sigma_D$ are totally excluded and so the reservoir of spheres is in equilibrium with a pure system of disks. This implies that the pressure of the nematic phase is equal to that of the sphere reservoir, and so above the triple point, the phase diagram follows the equa-

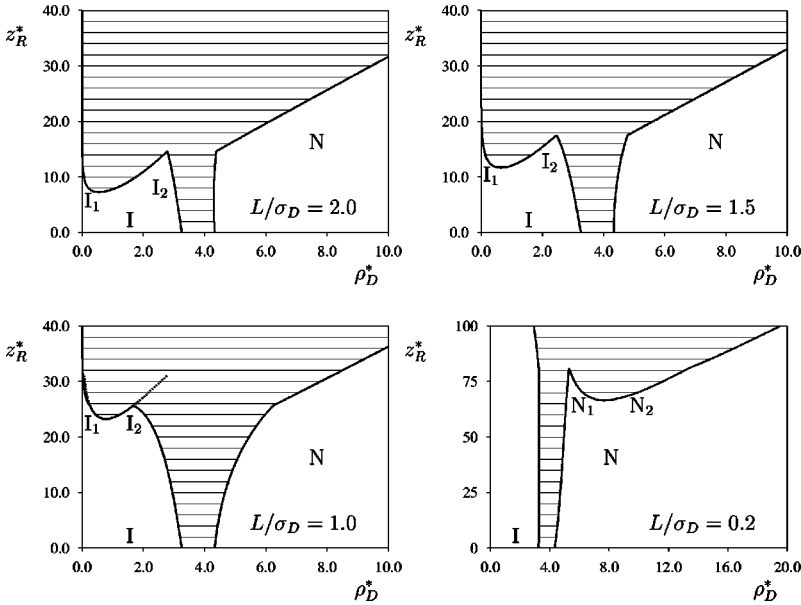


FIG. 4. Phase behavior of hard platelet and infinitely thin rod mixtures as predicted by perturbation theory as a function of platelet density ρ_D^* , and rod fugacity z_P^* , for various length-to-diameter ratios (L/σ_D).

tion $z_P^* = P^* = 3\rho_D^*$. While we cannot expect to obtain quantitative results, we can expect to get at least a qualitative view of the influence of polymer size on the phase behavior, since the major features of the phase diagram are predicted correctly using the perturbation theory. This will be examined in the next section.

IV. DISCUSSION

The dependence of the phase behavior on polymer diameter is shown in Fig. 3. As the diameter is lowered from $0.6\sigma_D$ to $0.3\sigma_D$, the I_1I_2 critical point occurs at increasingly higher z_P^* , while the platelet density at the critical point shifts to very slightly higher values. The critical point disappears, or rather becomes metastable with respect to NI coexistence, for smaller spheres. Since the perturbation theory does not reproduce the simulation results exactly, we cannot determine the exact size at which I_1I_2 coexistence is lost. However, from our previous observation that the theory predicts a critical point at too low z_P^* (see also Fig. 1), we expect that this will be in the region $0.3\sigma_D < \sigma_p < 0.4\sigma_D$. Decreasing the polymer size also has a profound influence on the width of the NI transition; this is dramatically widened as σ_p is reduced. This broadening has also been observed in experiments of mixtures of Gibbsite platelets with added polymer [22].

Bolhuis and Frenkel [23] have shown that hard spheres with a sufficiently short-ranged square well attraction undergo an isostructural solid-solid transition at high densities. We may wonder if a similar transition can occur in the platelet-polymer mixture for small polymer coils, since these induce a depletion force with a smaller range. This is indeed the case, and we find that a nematic-nematic (N_1N_2) coexistence is predicted by the perturbation theory for small polymer coils (see Fig. 3, $\sigma_p/\sigma_D = 0.06$ and 0.08). However, this occurs at very high densities, with the N_2 phase at densities of $\rho_D^* \approx 30$ and above, which is too high to be systematically investigated in the present simulations, let alone in an experiment. Moreover, at these high densities, we may expect that the N_1N_2 coexistence in systems of real (finite thickness)

platelets will become metastable with respect to other phases such as the columnar or solid phases, which only appear in the phase diagram of infinitely thin disks at infinite density [24].

While this appears to rule out nematic-nematic coexistence in colloid plus polymer systems, it may be possible to observe an N_1N_2 transition if a nonspherical depleting agent is used. To investigate this we have determined the free volume fraction α for infinitely thin rods of length L in a system of infinitely thin disks. The phase behavior resulting from the perturbation theory with this as input is shown in Fig. 4. For long rods, behavior similar to large spheres is found. Thus, I_1I_2 coexistence is observed with a critical point that shifts to higher z_P^* as the length of the rod is decreased until it becomes metastable with respect to the NI transition; the NI transition is also broadened with decreasing L . We also observe nematic-nematic coexistence for shorter rods (see Fig. 4, $L = 0.2\sigma_D$). However, while the N_2 phase was observed at extremely high platelet density for platelet-polymer mixtures, for platelet-rod mixtures it can occur at $\rho_D^* < 10$, which is just double the platelet density at the NI transition in the pure system. This may mean that it is possible to find N_1N_2 coexistence in experimental systems, although this coexistence may or may not be stable with respect to the transition to a columnar phase. This could be investigated in a simulation by studying the cut-sphere model that does exhibit a columnar phase instead of infinitely thin platelets. We also note that the present system could be thought of as a model for the recent experiments of mixtures of colloidal disks and rods [19], in which demixing of the system into discotic (N^-) and calamitic (N^+) nematic phases occurs. However, since the rods have zero excluded volume and they do not interact, they cannot self order to form a nematic phase and so we do not reproduce the behavior observed in the experiments. Coexistence between the I_1 and I_2 isotropic phases was not observed in the experiments of rods and plates. This is not surprising since the length of the rods was smaller than the diameter of the platelets, and the I_1I_2 coexistence is predicted to disappear for values of L below σ_D (see Fig. 4).

V. CONCLUSIONS

In conclusion, we have studied the influence of free non-adsorbing polymer on the phase behavior of colloidal platelets using computer simulation and perturbation theory. We find evidence for an I_1I_2 demixing transition within the isotropic phase for reasonably large polymer coils. As the polymer size is reduced, the I_1I_2 critical point becomes metastable with respect to the NI transition. For very small polymers, demixing in the nematic phase is possible although this occurs at extremely high densities. Similar behavior is observed for mixtures of very thin rods and platelets. However, in this case the N_1N_2 critical point occurs at experimentally accessible densities. Recent experiments on platelet-rod and platelet-polymer systems show a rich variety

of (liquid crystalline) phases, and so these should continue to provide a challenge for simulation and theory in the high-density regime. We have made a start toward understanding the behavior of these systems and the results obtained in this paper should provide a guide for experiments and give a useful testbed for future simulation and theoretical work.

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